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DEVELOPMENT OF CARBON/CARBON COMPOSITES WITH THROUGH-THICKNESS CARBON NANOTUBES FOR THERMAL AND STRUCTURAL APPLICATIONS

Zhiyong (Richard) Liang and Chuck Zhang

Florida A&M University

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14. ABSTRACT
Carbon/carbon composites offer lightweight thermal protection capable of producing excellent thermal materials. To further improve the thermal conductivity along the thickness direction and the interlaminar shear strength, we studied and demonstrated a novel method to stitch carbon nanotube yarns along the through-thickness direction of carbon fiber two-dimensional precursor felt perform to make novel 3D reinforced carbon/carbon (C/C) composites. By stitching nanotube yarns, high strength and thermal conductive CNTs were incorporated into the preform to significantly reinforce and improve thermal conductivity along the thickness direction. In this study, we illustrated the effectiveness of the stitching method to improve through-thickness conductivity (Kz) through both modeling estimations and experimental studies. The C/C composites with 1wt.%-8wt.% stitched nanotube yarns were fabricated using in situ densification process with T300 plane weave precursors. The through-thickness conductivity measurements results using a laser-flash method showed the Kz values of the C/C composites samples with stitched nanotube yarns had large variations. The C/C composite samples with 8wt.% stitched nanotube yarns showed a Kz as high as 24.5W/mK, which was approximately a 44 percent increase compared to 17 W/mK conductivity of the control sample. The Rule of Mixture estimated the conductivity of the nanotube yarns is possibly in the range of 110W/mK through 375W/mK. Scanning electron microscopy (SEM) and Raman analysis also proved that the nanotubes survived after consolification and carbonization processing temperatures of 2500 to 2800 °C. These results demonstrate the feasibility of using stitched nanotube yarns to effectively improve through-thickness conductivity.

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C/C composites, thermal conductivity, nanotubes

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1. Introduction

Carbon/carbon composites offer lightweight thermal protection capable of producing excellent thermal materials. To further improve the thermal conductivity along the thickness direction and the interlaminar shear strength, we studied and demonstrated a novel method to stitch carbon nanotube yarns along the through-thickness direction of carbon fiber two-dimensional precursor felt perform to make novel 3D reinforced carbon/carbon (C/C) composites. By stitching nanotube yarns into precursor performs during the C/C composite manufacturing processes, high strength and thermal conductive nanotubes (CNTs) can be directly incorporated into the preform to significantly reinforce and improve thermal conductivity along the thickness direction. Particularly, the stitching approach provides essential continuity, alignment and high concentration to effectively utilize nanotubes' exceptional properties. Furthermore, the success of the proposed approach could provide an effective method for scale-up and affordable production carbon/carbon composites using nanotube materials.

2. Objectives and Goals

The primary objectives of the research was to develop a novel manufacturing process to improve the thermal conductivity along thickness direction and the interlaminar shear strength of 2D felt or preform based carbon/carbon composite by effectively introducing through-thickness CNT materials using a stitching method. In the reporting period (first year effort), we focused on material selection and feasibility study through both modeling and experimental efforts. The detail project objectives included:

- Identify and obtain nanotube yarn or electrospinning nanofiber materials suitable for stitching process;
- Develop the nanotube yarn titching process in the thickness direction at 2D precursor perform of PAN-fiber felts;
- Fabricate the C/C composite samples with different stitching densities of nanotube yarns;
- Evaluate the properties of the resultant c/c composite: thermal conductivity in the thickness direction, nano/microstructures, and possible oxidation and thermal degradation of nanotubes during densification and graphitization processes;
- Model the effects of through-thickness nanotube on thermal conductivity of the resultant stitched C/C composite samples;

- Attend required review meetings, send students to brief project progress, and prepare technical reports.

3. K_z and Stitching Parameter Predictions of CNT Yarn Stitching

K_z and stitching parameters of CNT Yarn stitched C/C composites were modeled using the Rule of Mixture first based on literature information and yarn property provided by the vendor (Nanocomp, NH). The major assumptions and parameters used are listed below:

- Continuous CNT Yarn from Nanocomp Technologies Inc. was used to stitch C/C composites.
- The as-received CNT Yarn was a 3Tex filament, which was 3 grams per kilometer long. The yarn density was assumed as 1.33 g/cm^3. With this information, the calculated radius of the yarn was at 26 microns.
- The thermal conductivity of the CNT yarn was unknown; values between 200-600 W/mK were assumed.
- Due to the extremely small radius of as-received CNT yarn or filament, multiple yarn filaments were used to make a twisted stitching yarn to achieve a stitchable radius and practical stitching densities in the modeling.

The following equations were used for the predictions. Table 1 lists the material parameters.

$$K_{eff} = K_{cc} \cdot (1 - V_f) + K_y \cdot V_f$$

$$V_f = \frac{n \cdot \pi r^2 \cdot h}{A_t \cdot h} \Rightarrow n = \frac{A_t \cdot V_f}{\pi r^2} \qquad (1)$$

$$D = \sqrt{\frac{\pi r^2}{V_f}}$$

K_{eff} –Effective Conductivity (K_z)	K_{cc} – C/C composite through-thickness Conductivity
K_y – CNT Yarn Conductivity	V_f – Yarn Volume Fraction
A_t – Stitching Cross-Section Area	D – Center to Center Stitch Distance of CNT Yarn
n – Number of Yarn Stitches	r – Radius of Stitching Yarn of multiple CNT yarn Filaments

Table 1. Calculation of stitching parameters

K_y (W/mK)	K_{cc} (W/mK)	ρ_y (g/cm^3)	ρ_{cc} (g/cm^3)	Yarn radius (r) (mm)	Number of yarn filaments to make a twisted stitching yarn
200	30	1.33	1.8	0.2144	8x
300	30	1.33	1.8	0.1072	4x
400	30	1.33	1.8	0.0536	2x
500	30	1.33	1.8	0.0268	1x
600	30	1.33	1.8		

Based on the yarn size and material density values, Figures 1 and 2 show the predicted relationships of stitching density and yarn volume fraction, respectively. The radius of the as-received yarns was too small to conduct a practical stitching process. Large size stitching yarns were made by combining 4-10 yarns together through twisting or chemical binding to make stichable yarns or tows for achieving at least 5-10v% CNT yarn content. The K_z with stitching yarns were also projected using the Rule of Mixture. Figures 3 and 4 show the results indicating that 10v% CNT yarns with 600W/mK conductivity, can achieve about 90 W/mK, which is about three times the typical K_z value of 2D C/C composites. The stitching distance was about 1mm to each other using the twist nanotube yarn, which was feasible for actual stitching process. We performed stitching experiments based on the prediction results to prepare stitched samples with 5-10v% CNT yarn content. The model results show that the through-thickness conductivity of C/C composites can be effectively and practically improved using stitched high conducting nanotube yarns.

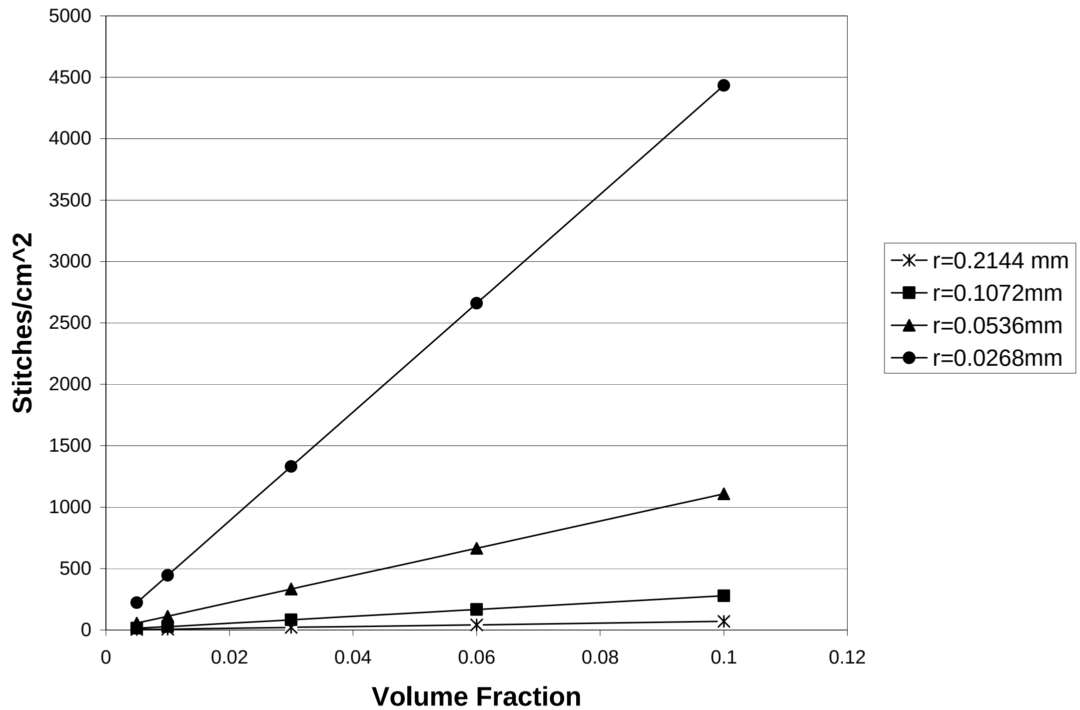


Figure 1. Stitches per cm^2 vs. volume fraction of the CNT yarns depending on the radius of twisted stitching yarn of multiple CNT yarn filaments

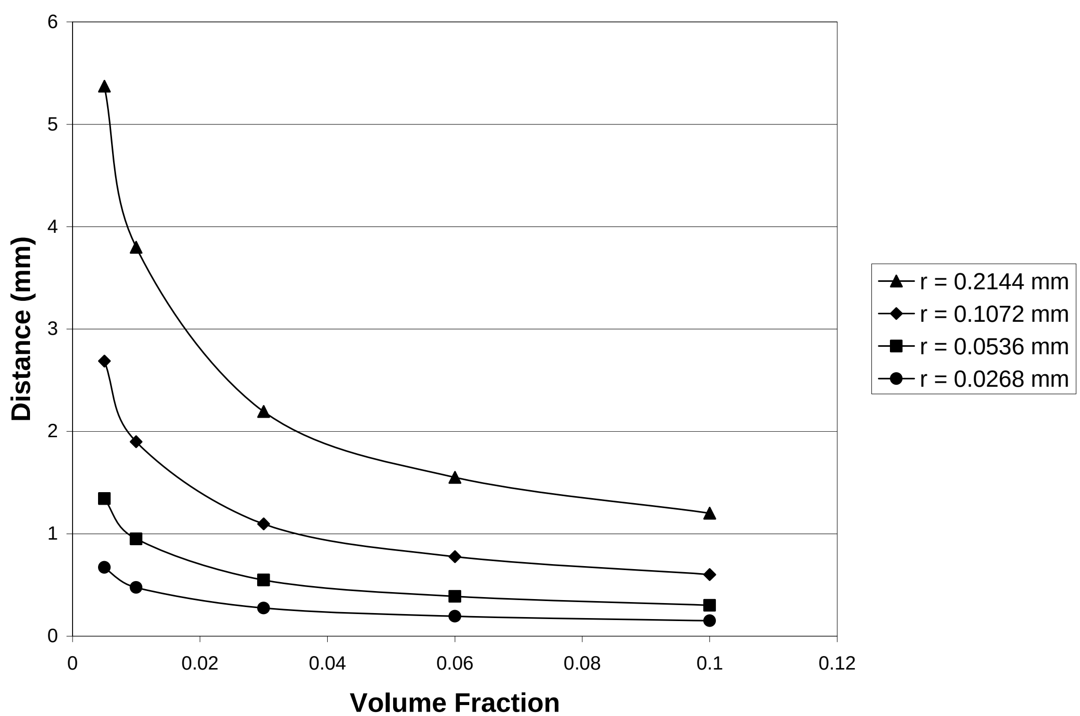


Figure 2. Center to center stitch distance vs. volume fraction depending on the radius of twisted stitching yarn of multiple CNT yarn filaments

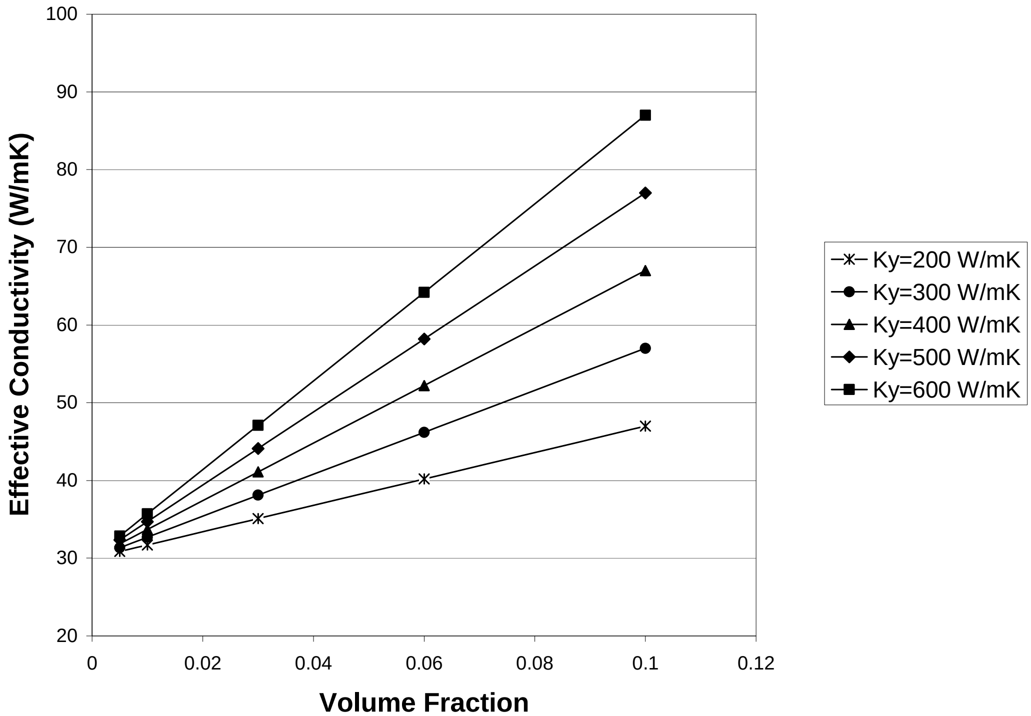


Figure 3. Effective conductivity vs. volume fraction of stitched CNT yarns depending on CNT yarn conductivity

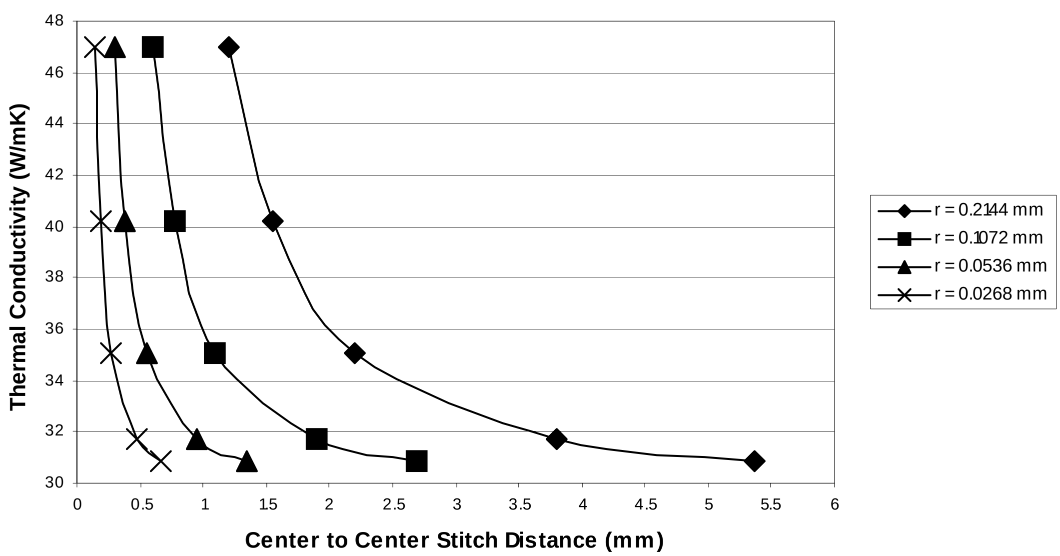


Figure 4. Thermal conductivity vs. center to center stitch distance depending on CNT yarn stitch radius and yarn conductivity of 200 W/mK

4. Characterization of Nanotube Yarns

The CNT yarn used in this research was supplied by Nanocomp. The yarn was a 3Tex filament, which according to the vendor's datasheet was 3 grams per kilometer long. Validation experiments were carried to reveal basic properties of the yarns using SEM, Raman analysis and mechanical property tests. Based on the characterization results, we updated the stitching sample designs and parameters.

4.1 Tensile properties of Nanocomp nanotube yarns

Through tensile properties tests using a DMA machine (Model 2980, TA Instrument), we tested the yarn samples to confirm Nanocomp's claims of mechanical properties. Five group tests were conducted on the samples of 1 inch long and 70 microns in diameter. The diameters were confirmed by SEM analysis (see Section 4.3). Figure 5 shows typical test curves. Table 2 lists the results of the DMA test results of the five group tests from two batches of the CNT samples. The yarn materials demonstrated relatively high mechanical properties, but large property variations were also seen. Our test results showed lower results than reported data from the vendor.

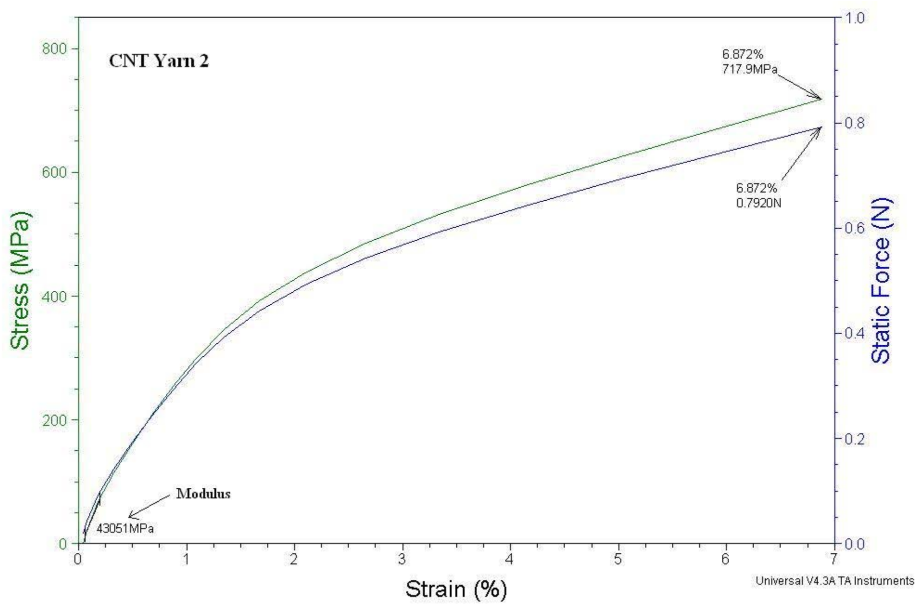


Figure 5. Tensile tests of CNT Yarns

Table 2. CNT yarn tensile properties

Sample	Stress (MPa)	Static Force (N)	Strain (%)	Modulus (GPa)
CNT Yarn 1	205.5	0.8125	2.0	24.748
CNT Yarn 2	717.9	0.7920	6.9	43.051
CNT Yarn 3	242.3	0.9819	7.0	12.187
CNT Yarn 4	153.7	0.6422	5.1	8.655
CNT Yarn 5	212.3	0.8670	9.6	16.191

4.2 Raman analysis of nanotube yarns

A Raman spectrum analysis, using a Confocal Research Raman Microscopy (InVia, Renishaw), was conducted to reveal type of nanotubes in the nanotube yarns. Based on Nanocomp's datasheet, the nanotube yarn consists of a mixture of SWNTs and MWNTs. Figure 6 shows the presence of SWNTs by the Radial Breathing Mode (RBM), which indicates the existing SWNTs. However, due to the relatively large D band shown in Figure 6, we cannot rule out the existence of MWNTs. Our Raman analysis confirmed the composition of SWNTs and MWNTs in the CNT yarns.

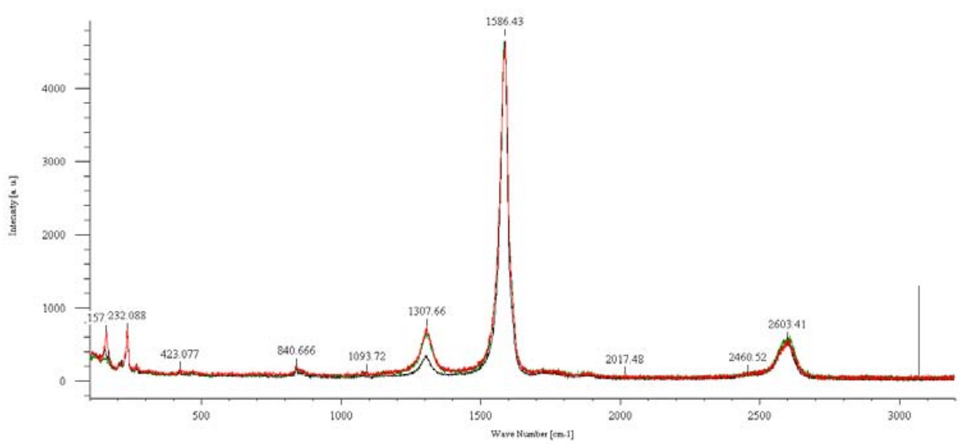


Figure 6. Raman analysis of CNT yarns

4.3 SEM analysis of nanotube yarns

SEM analysis of the nanotube yarns was conducted using a JEOL 7401 FE-SEM machine. Figures 7-10 show that the yarn was densely packed with aligned nanotubes, which is essential for improving through-thickness properties in the stitching process. It also confirmed the diameter of the as-received nanotube yarns was about 70 microns, as shown in Figure 7.

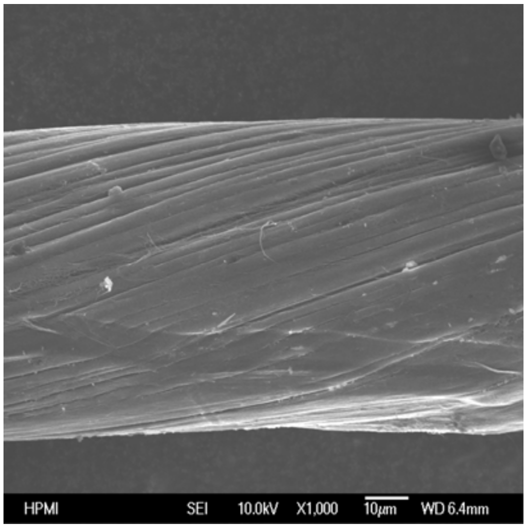


Figure 7. Yarn structure of twisted CNT bundles

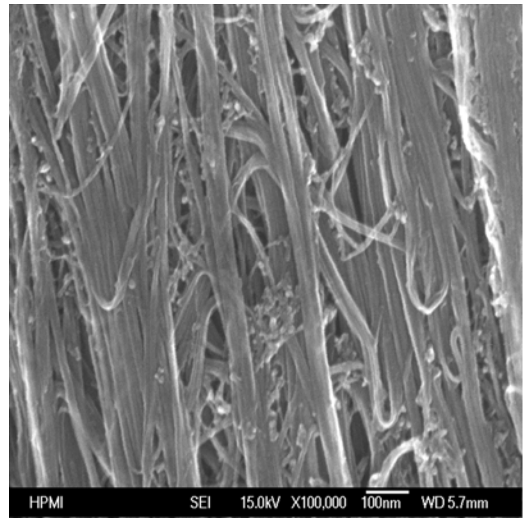


Figure 8. Aligned nanotube ropes along the yarn axial direction

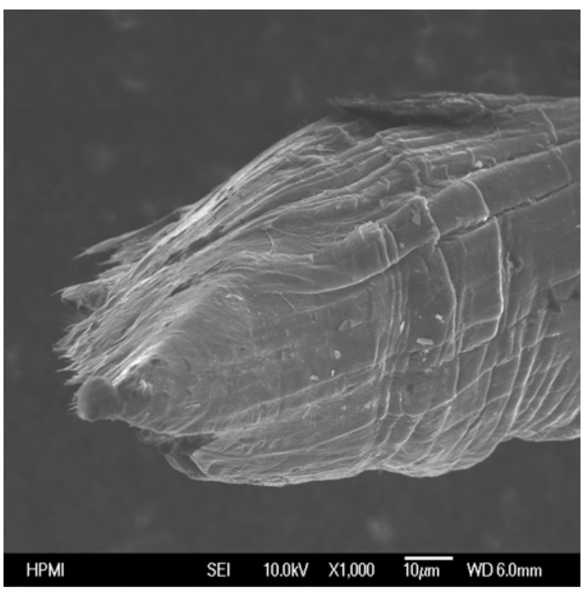


Figure 9. Fracture end of a nanotube yarn after test

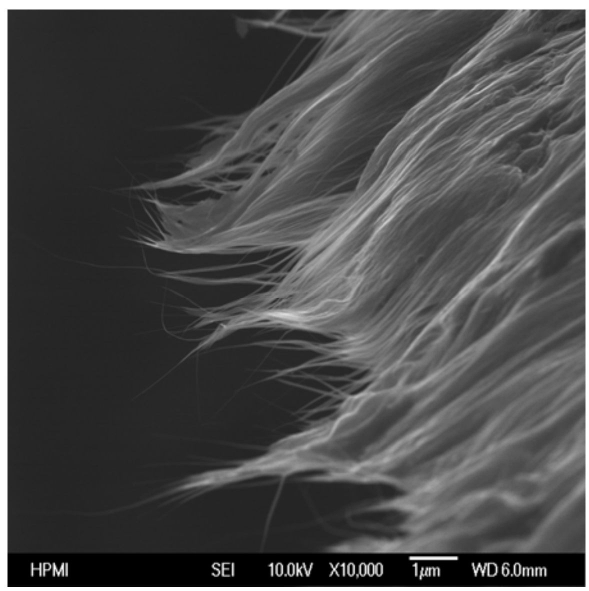


Figure 10. Nanotube breaks at the fracture end

4.4 Updated prediction of stitching parameters

Based on the measured diameters (70 microns) and density (0.7795 g/cm^3), the stitching parameters calculated in Section 3 were re-calculated and updated as shown in Figures 11-14. Based on these predictions, we planned to make the C/C composite samples with 1v%~15v%

stitching CNT yarns to study the effect of the nanotube yarns on Kz values of C/C composites. We assumed that the smallest radius of the stitching yarns was the twisted stitching yarns combining two as-received nanotube yarns with about 70 micron diameter.

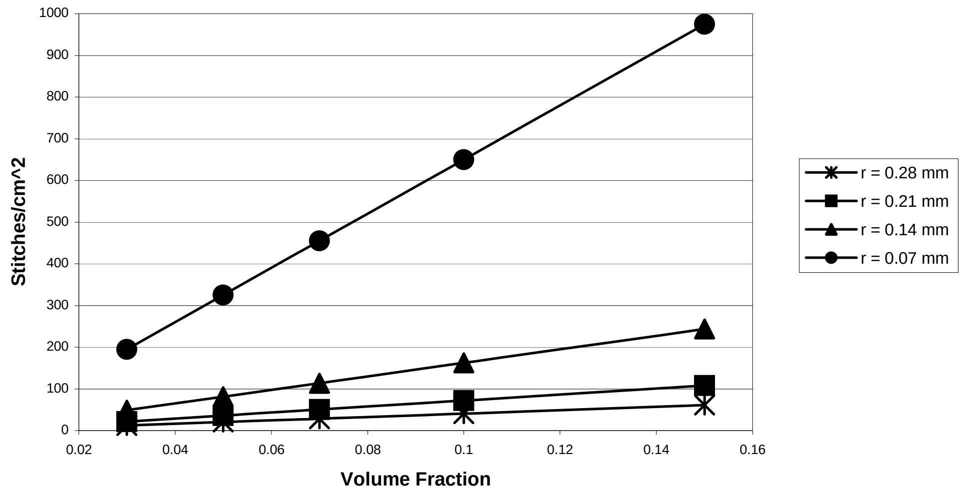


Figure 11. Stitches per cm^2 and CNT yarn volume fraction depending on twisted stitching CNT yarn radius

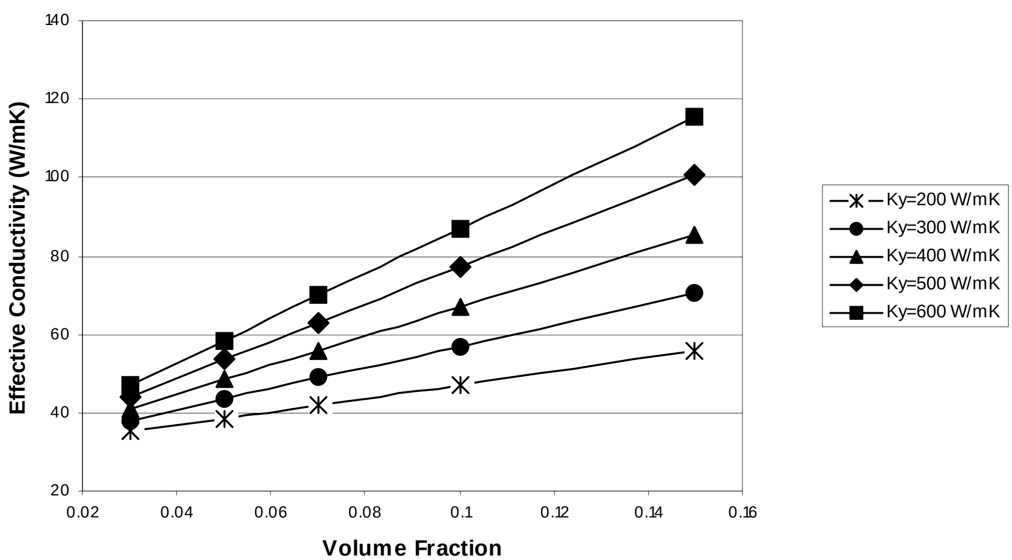


Figure 12. Effects of yarn conductivity and volume fraction on Kz of the C/C composite with stitched CNT yarns

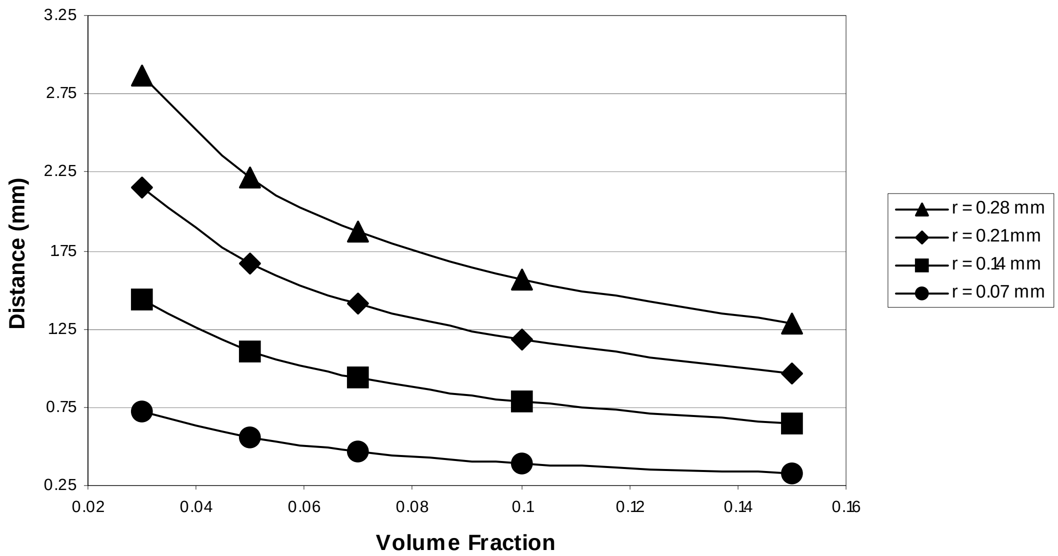


Figure 13. Center-to-Center stitch distance and stitching yarn volume fraction/twisted stitching CNT yarn radius (r)

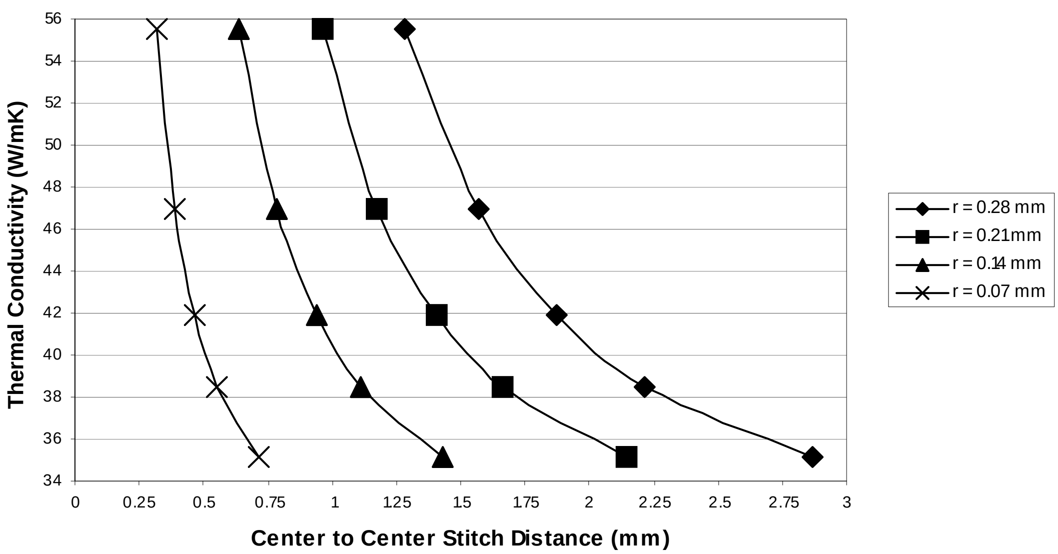


Figure 14. Thermal conductivity (Kz) vs. center-to-center stitch distance
(Depending on CNT yarn stitch radius and yarn conductivity of 200 W/mK)

5. Development of Stitching Process

The development of stitching process was divided into two steps to study the process using both copper wires and nanotube yarns with glassfiber/epoxy resin composites to develop basic stitching techniques and expertise and to conduct nanotube yarn stitching in precursor performs of C/C composites.

5.1 Stitching process of glass fiber composites with copper and nanotube yarns

In this research, the purpose of stitching process was to thread high conductive material throughout the entire composite thickness or only a desired portion of the composite thickness at the fiber preform and pregreg layup stages. To control stitching density, the stitch method was implemented after the materials to be stitched were layered and compressed. In the experiments, we first made a perform of three layers of E-glass fabric by using a 3M Super 77 Multipurpose Adhesive to hold the fabrics or any material assemblies to facilitate the stitching processes.

We conducted both manual and machine stitching techniques:

- Manual Stitch -- The hand stitching process is easy to use for making initial small samples, but it is relatively slow in production and lacks accuracy.
- Sewing Machine -- A sewing machine can be used to stitch the conductive materials similar to stitching layers of fabric for making clothes. The stitch distance can be adjusted. This process is faster in production and can accurately produce the stitch pattern desired. Programmable sewing machines, such as the Quantum XL-6000 by Singer with a desired pattern, can be used to automate the process. However, machine stitching process must use very flexible and high strength materials.

Due to the possible high stitching density required, we used the manual stitching method in our experiments. Different stitching patterns were also explored in the study. Figure 15 shows two stitching patterns tested to improve through-thickness thermal conductivity values in composites. The use of various materials may alter the stitching technique selection in a particular process. Metallic wires, such as copper, have a low tension strength and flexibility, which are not able to withstand the stress applied by the sewing machine in an over-and-under stitching pattern. A single through-stitch technique is performed where the yarn is cut after each stitch, which can be easily used for various materials. In this study, we used manual stitching method and single through-stitch patterns for both copper wires and nanotube yarns.

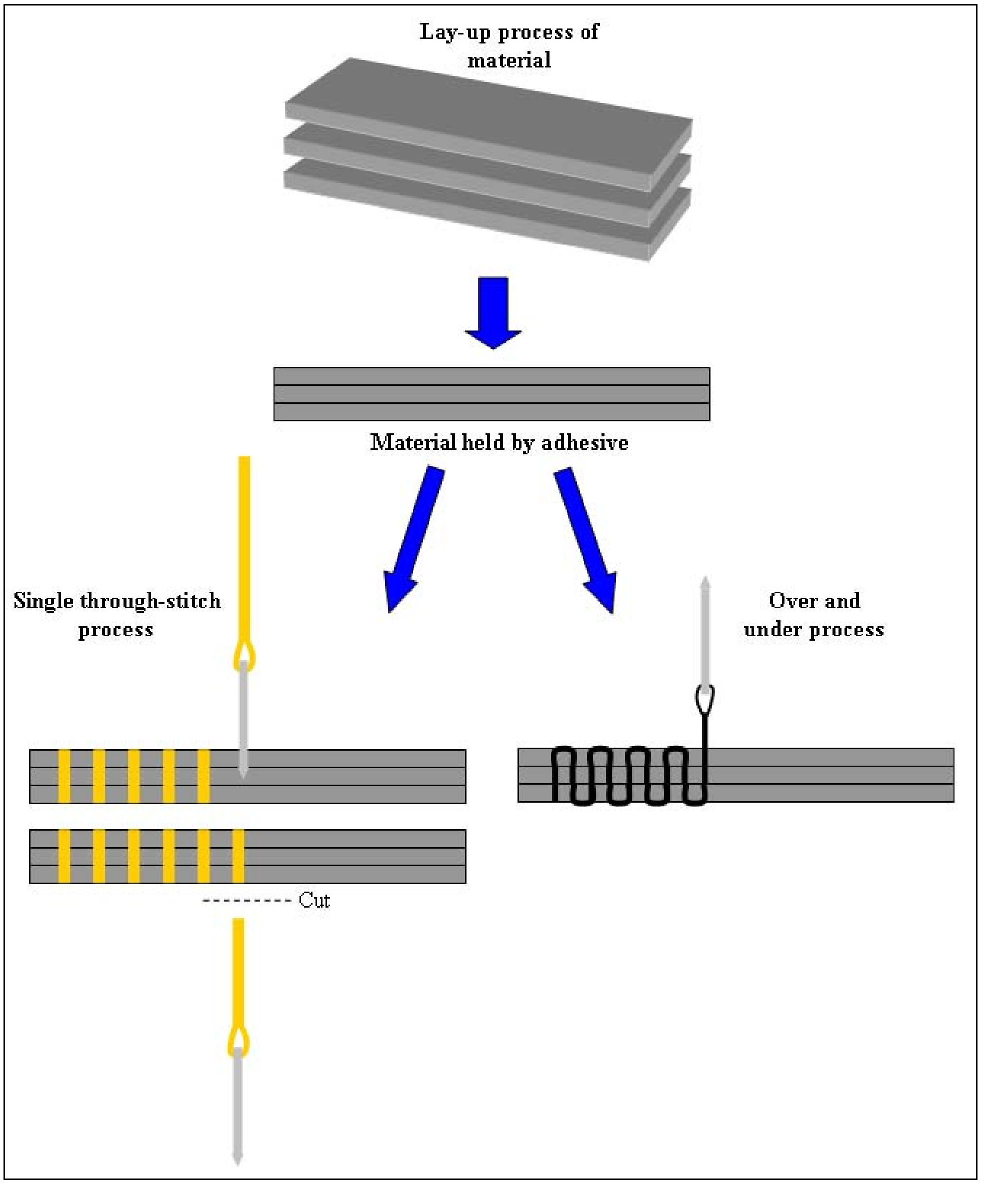


Figure 15. Two through-thickness stitching patterns: single through-stitch and over-and-under

Special attention is required to limit in-plane fiber material damage during the stitching process to eliminate large property reduction of the composites. In this experiment, a fine point needle was used. Dritz, Singer and Schemtz provided quilting embroidery needles that can be utilized with most composite materials. The fine point needle allows stitching through the weave of the fabric or material structure, causing a minimal amount of damage. After stitching, reinforcement fibers formed around the threaded material or stitching yarns, making as much contact as possible to facilitate thermal conductance. Figure 16 shows an image of a fiberglass fabric prefom samples with through-thickness stitched copper wires and CNT yarns. Figure 17 shows examples of cured glassfiber/epoxy composite samples with stitched copper wire (0.003 inch diameter) and nanotube yarns ready for thermal conductivity measurement.

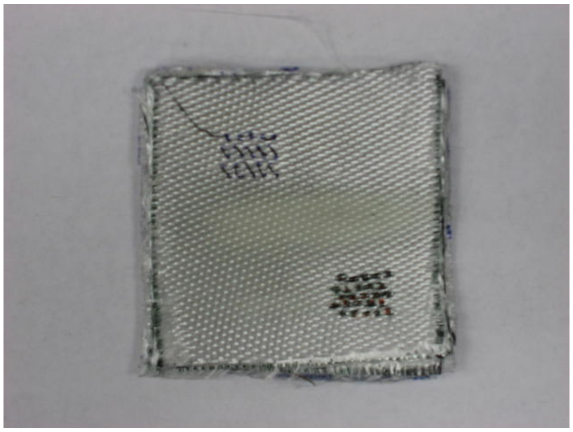


Figure 16. Glass fiber perform with different nanotube stitching density

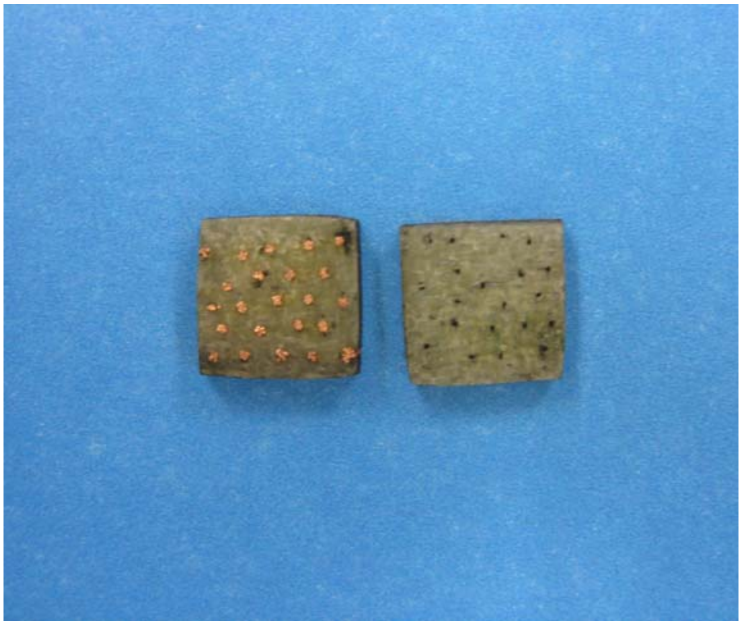


Figure 17. Cured glass fiber/epoxy composite samples with stitched copper wire (0.003 inch diameter) and nanotube yarns ready for thermal conductivity measurement

Three sets (Set 1, 2 and 3) of glassfiber/epoxy composites with stitched copper and nanotube yarn were fabricated to reveal the feasibility and repeatability of stitching process and Kz enhancement. The resultant samples were tested using a Netzsch LFA 457 Microflash machine to provide the thermal diffusivity results. Table 3 shows the test results. Taking the thermal diffusivity (α), specific heat (cp), and density (ρ) of the samples, the thermal conductivity (k) were determined using the formula:

$$k(T) = \alpha(T) \bullet cp(T) \bullet \rho(T) \quad (2)$$

The specific heat used was 0.81 J/gK.

Table 3. Kz enhancement of stitched glass fiber/epoxy composites

Samples and Stitching Yarn Volume Fraction	Density (g/cm^3)	Thickness (mm)	Diffusivity (avg. mm^2/s)	Thermal Conductivity (W/mK)
Set 1: CNTY 0.4% V_f	1.903	2.08	0.25	0.38
Set 1: Cu 1.8% V_f	2.052	2.4	0.9	1.48
Set 2: CNTY 0.4% V_f	1.798	2.3	0.27	0.39
Set 2: Cu 1.8% V_f	1.91	2.65	0.95	1.45
Set 3: CNTY 0.4% V_f	1.943	1.96	0.3	0.47
Set 3: Cu 5.0% V_f	1.987	2.4	3.7	5.88
Set 3b: Cu 5.0% V_f	2.03	2.4	5.0	8.12
Control Samples	1.985	2.3	0.18	0.29

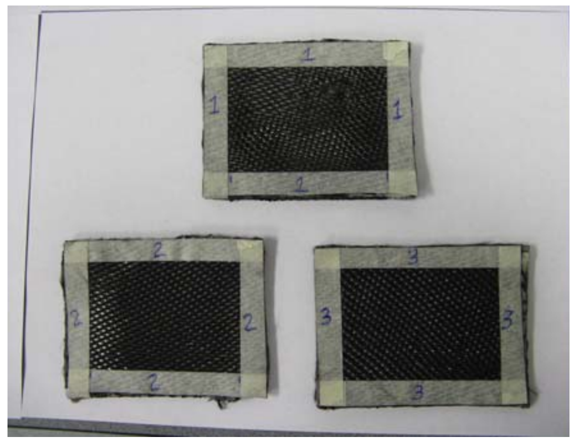
The results show that the developed stitch method increases the through-thickness thermal conductivity (Kz) considerably while making a negligible difference in the overall composite density due to the limited amount of the stitching material used. The varying difference of the sample density can be contributed to the possible glassfiber volume variations in the samples, but the difference between each sample is negligible. The thermal diffusivity results from the samples with same stitching yarn fraction show noticeable variability, but there was a consistent trend of Kz increase due to high conducting material stitching.

The samples stitched with a nominal amount of the CNT yarn were of interest. Though it is hard to ascertain the exact thermal conductivity of the CNT yarn, the percentage used resulted in roughly a 50% increase of Kz of the composites. Sample Set 3 proved that the experimental results can be repeated and confirms that the results from Set 3 of the 5.0% V_f of stitched copper wires. The outcome shows a 27-fold increase in through-thickness thermal conductivity for fiberglass composites with 5.0% V_f of stitched copper wires, which is significant.

5.2 Fabrication of stitched heat-treated T300 carbon fiber precursors

We used heat-treated T300 fabrics from Allcomposite (CA) and 30 meters of nanotube yarn (37-87 microns in diameters by SEM analysis) from Nanocomp to prepare final reinforcement perform precursors for C/C fabrication. Figure 18 shows the preforms of two control samples and three stitched samples (3v%, 5v% and 7v% stitching nanotube yarns) produced. The samples were 2 in x 3 in.

(a) Preforms of heat-treated T300 fabrics with applied processing adhesives



(b) Nanotube yarn stitched performs (12 layers of fabrics with 3v%, 5v% and 7v% stitched nanotube yarn

Figure 18. Preparation of the control and stitched T300 fabric precursors

The size of Kz test samples were 10mm x 10mm, which were cut from each 2 in x 3 in C/C composite sample, as shown in Figure 19. A total of 18 samples were tested as described in Table 4. Six types of the samples were stitched with various concentrations of carbon nanotube (CNT) yarns and were cut into the 10mm x 10mm size for thermal tests after C/C composite fabrication. The concentration of CNT in the six stitched samples ranged from 1.04v% to 13.7v%. Twelve control samples were also cut from the corresponding C/C composite panel, as shown in Table 4 and Figure 19. The results from the corresponding controlled and stitched samples were compared to reveal the effects of stitched CNT yarns on the Kz values. The diameters of the nanotube yarns were actually measured values. The V_f of the stitching yarn was calculated based on Equation 1.

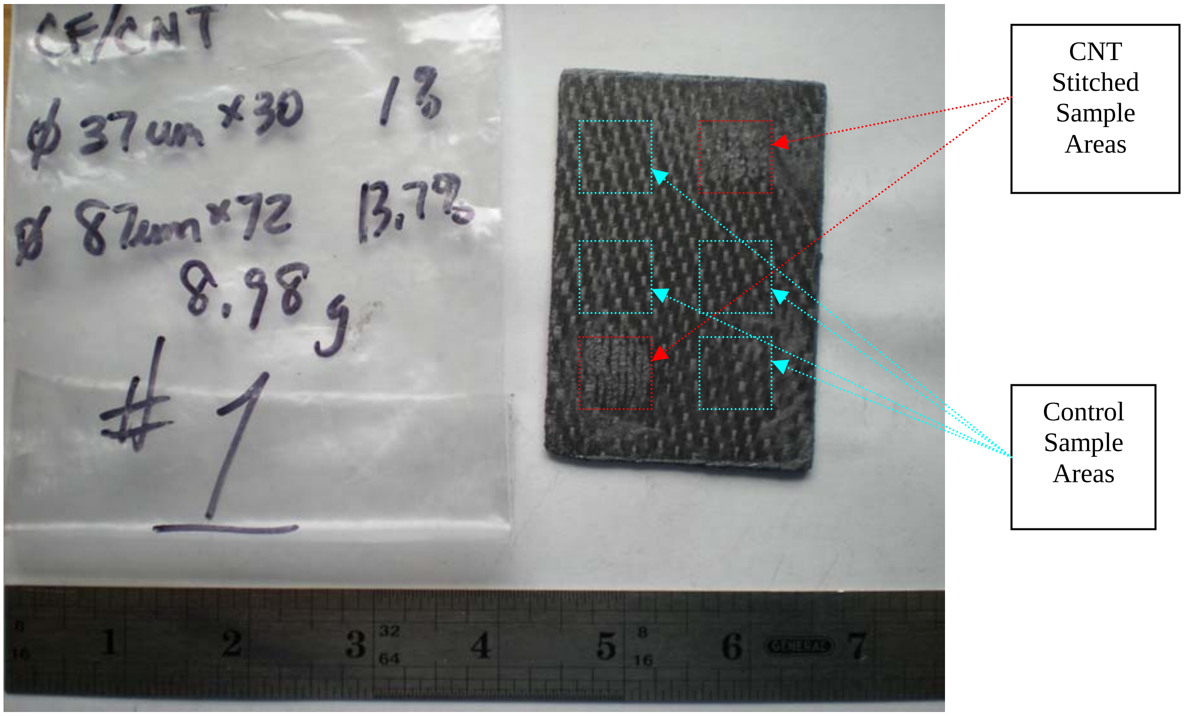


Figure 19. Preparation of control and stitched C/C composite precursor performs

Table 4. Parameters of precursor preforms of the C/C composite samples

Samples	Description	CNT Yarn Diameter (μm)	Stitching Yarn Volume Fraction	Stitches/cm^2
Stitched 1a	Carbon Fiber (CF)/CNT Yarn	37	1.0%	30
Stitched 1b		87	13.7%	72
Control 1a	C/C	0	0	0
Control 1b				
Stitched 2a	CF/CNT Yarn	84	5.3%	30
Stitched 2b		87	8.2%	43
Control 2a	C/C	0	0	0
Control 2b				
Stitched 3a	CF/CNT Yarn	84	2.8%	16
Stitched 3b		70	11.6%	94
Control 3a	C/C	0	0	0
Control 3b				

5.3 Fabrication of C/C composites with stitched nanotube yarns

C/C composite fabrication was conducted by Allcomp, using its proprietary *in-situ* CVD and densification process to produce the stitched carbon/carbon (C/C) composite samples. The major processing and material parameters are listed as follows:

- Estimated carbon fiber volume was 60v%;
- Density of the resultant C/C composite samples ranged from 1.51-1.57 g/cc after 2 densification cycles;
- Heat treatment temperature >2800 °C at the end of the process.

As planned in Section 5.2, each stitched and controlled sample was cut into 10mm x 10mm squares for thermal conductivity testing. However, the designed dimensions of the stitched areas in the samples were changed after C/C composite fabrication process. The *in situ* densification process was the probable cause of perform compression and expansion of stitched area. Therefore, the original designed volume fractions of the stitched nanotube yarns (see Table 4) must be re-calculated based on the stitching area dimension changes, as shown in Figure 20. Table 5 summarizes the final volume fractions of the stitched nanotube yarns in each C/C sample.

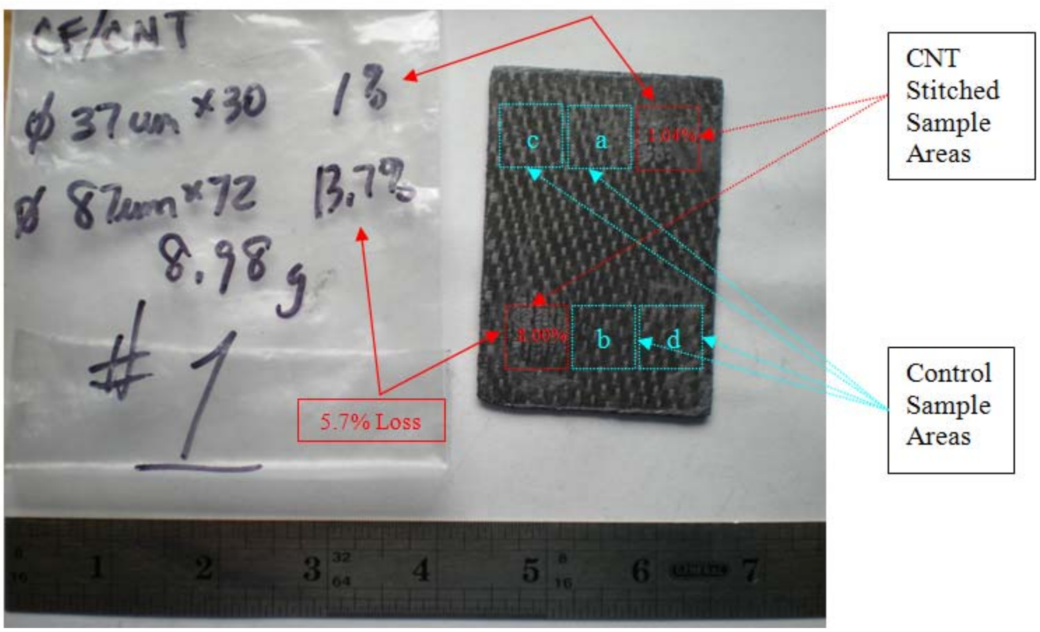


Figure 20. Actual volume fractions of the stitched nanotube yarns in the C/C composites samples

6. Kz Measurements and Result Discussion

Once each sample of thermal conductivity test was cut to the 10 mmx10 mm size, measurements for density and diffusivity were conducted. Table 5 provides the results.

Table 5. Volume Fraction of stitched nanotube yarn and densities of the resultant C/C composites

Samples	Stitched Sample (%)	Density (g/cm^3)
Panel 1	1.04	1.58
	8.0	1.53
Panel 2	5.72	1.46
	3.55	1.50
Panel 3	2.84	1.51
	5.91	1.45

6.1 Density test

Density tests were conducted in accordance with ASTM standard D792-00 to check and confirm the Allcomp's data. This standard determines the ratio of a C/C composite weight in air with respect to its weight in distilled water. The ratio was multiplied with the density of distilled water to determine the density of the C/C composite samples. A comparison of Tables 5 and 6 show that the stitched samples have lower density values, and the controlled samples close to the stitched areas were less dense. A possible reason is due to the stitches deforming the layers of carbon fiber in the performs, resulting in more amorphous carbon and void formations in the stitching areas.

6.2 Diffusivity measurements

The Netzsch LFA 457 laser flash machine was used to measure the thermal diffusivity of the samples to calculate the thermal conductivity. The tests were conducted in accordance with ASTM E-1461. The test temperature ranges was set as RM-250°C. Tables 7-9 list the diffusivity values based on three measurements taken at an approximate temperature. The three measurements and temperature were averaged and the standard deviation was calculated.

Table 6. Densities of the C/C composite Control Samples

Samples	Controlled Samples	Density (g/cm^3)	Avg. Density (g/cm^3)
Panel 1	1a	1.63	1.64
	1c	1.65	
	1b	1.62	1.64
	1d	1.66	
Panel 2	2a	1.58	1.61
	2c	1.63	
	2b	1.60	1.62
	2d	1.65	
Panel 3	3a	1.63	1.62
	3c	1.60	
	3b	1.62	1.61
	3d	1.60	

Table 7. Diffusivity values of samples on Panel 1

	CNT (Volume Fraction)	Temp (°C)	Diffusivity (mm^2/s)	Std. Dev.	Control Sample	Temp (°C)	Diffusivity (mm^2/s)	Std. Dev.
Panel 1	.0104	26.6	18.328	.065	1a	26.4	14.751	0.036
	.0104	40.6	17.092	.033	1a	40.8	13.835	0.105
	.0104	59.4	15.72	.118	1a	59.6	12.823	0.125
	.0104	78.6	14.672	.09	1a	79	11.921	0.012
	.0104	100.6	13.753	.095	1a	100.7	11.076	0.016
	.0104	149.6	11.709	.069	1a	151	9.27	0.004
	.0104	199	10.098	.044	1a	200.1	8.044	0.015
	.0104	26.7	18.501	.038	1c	26.7	14.32	0.028
	.0104	41.1	17.235	.085	1c	41.6	13.359	0.074
	.0104	59.4	15.857	.171	1c	60.1	12.429	0.134
	.0104	79	14.834	.024	1c	78.9	11.489	0.02
	.0104	100.9	13.851	.133	1c	99.5	10.833	0.025
	.0104	150.6	11.675	.043	1c	149.5	9.212	0.01
	.0104	200.1	10.124	.009	1c	199.6	7.909	0.007
	.08	26.7	22.638	.091	1b	26.6	14.772	0.088
	.08	41.2	20.947	.109	1b	40.9	13.808	0.046
	.08	59.2	19.476	.13	1b	60.1	12.848	0.064
	.08	78.6	18.139	.11	1b	79.1	11.948	0.054
	.08	100.9	17.086	.134	1b	100.3	11.111	0.027
	.08	151	14.549	.043	1b	150.1	9.384	0.023
	.08	200.6	12.642	.037	1b	200.2	8.04	0.031
	.08	26.6	22.198	.121	1d	26.4	14.365	0.088
	.08	40.8	20.705	.107	1d	41.6	13.392	0.078
	.08	59.4	19.052	.076	1d	59.9	12.48	0.06
	.08	79	17.854	.078	1d	79.6	11.599	0.076
	.08	100.7	16.661	.096	1d	99.8	10.891	0.016
	.08	150.6	14.19	.065	1d	149.6	9.23	0.018
	.08	199.9	12.347	.013	1d	199.6	7.928	0.01

Table 8. Diffusivity values of samples on Panel 2

	CNT (Volume Fraction)	Temp (°C)	Diffusivity (mm^2/s)	Std. Dev.	Control Sample	Temp (°C)	Diffusivity (mm^2/s)	Std. Dev.
Panel 2	0.0572	26.4	15.942	0.111	2a	26.3	14.916	0.048
	0.0572	40.9	14.981	0.052	2a	41.2	13.844	0.058
	0.0572	59.6	13.939	0.057	2a	59	12.913	0.047
	0.0572	79	13.147	0.035	2a	79.4	12.059	0.029
	0.0572	100.1	12.372	0.046	2a	100	11.17	0.19
	0.0572	148.4	10.781	0.008	2a	148.9	9.534	0.019
	0.0572	200.5	9.492	0.02	2a	199.5	8.129	0.034
	0.0572	26.7	15.941	0.253	2c	41.4	12.474	0.037
	0.0572	41	14.954	0.022	2c	60	11.657	0.108
	0.0572	58.9	13.871	0.03	2c	79.2	10.869	0.03
	0.0572	79.1	13.064	0.057	2c	100.3	10.134	0.187
	0.0572	100.1	12.303	0.031	2c	149.5	8.674	0.033
	0.0572	149.2	10.712	0.023	2c	199.4	7.45	0.019
	0.0572	200.4	9.441	0.025	2b	26.6	15.094	0.032
	0.0355	26.6	15.806	0.018	2b	41.4	14.106	0.05
	0.0355	40.7	14.794	0.044	2b	59.7	13.045	0.105
	0.0355	59.4	13.736	0.078	2b	79.3	12.21	0.073
	0.0355	81.3	13.052	0.338	2b	99	11.203	0.078
	0.0355	101	12.158	0.085	2b	150.2	9.529	0.057
	0.0355	150.8	10.537	0.08	2b	200.5	8.226	0.021
	0.0355	200.8	9.227	0.049	2d	26.7	13.068	0.526
	0.0355	26.6	15.051	0.054	2d	26.5	14.127	0.132
	0.0355	40.9	14.074	0.03	2d	41.5	13.12	0.147
	0.0355	59.3	13.045	0.046	2d	59.5	12.143	0.048
	0.0355	78.9	12.212	0.04	2d	79.4	11.336	0.067
	0.0355	100.5	11.437	0.019	2d	100.9	10.66	0.075
	0.0355	149.1	9.88	0.017	2d	149.4	9.007	0.013
	0.0355	200.1	8.651	0.01	2d	200.6	7.714	0.026

Table 9. Diffusivity values of samples on Panel 3

	CNT (Volume Fraction)	Temp (°C)	Diffusivity (mm^2/s)	Std. Dev.	Control Sample	Temp (°C)	Diffusivity (mm^2/s)	Std. Dev.
Panel 3	0.0284	26.6	12.012	0.039	3a	26.7	14.393	0.049
	0.0284	40.7	11.277	0.023	3a	41.4	13.488	0.091
	0.0284	59.2	10.488	0.061	3a	59.8	12.592	0.037
	0.0284	78.7	9.838	0.066	3a	79	11.637	0.059
	0.0284	100.6	9.286	0.056	3a	99.4	10.792	0.071
	0.0284	150.9	8.057	0.051	3a	150.1	9.184	0.019
	0.0284	199.4	7.049	0.011	3a	200.5	7.928	0.025
	0.0284	26.6	12.02	0.064	3c	26.7	14.805	0.037
	0.0284	40.7	11.29	0.058	3c	41.4	13.855	0.064
	0.0284	59.3	10.501	0.049	3c	60.1	12.778	0.112
	0.0284	78.7	9.852	0.059	3c	79.3	11.972	0.038
	0.0284	100.6	9.302	0.072	3c	99.7	11.105	0.035
	0.0284	150.8	8.014	0.02	3c	149.1	9.435	0.018
	0.0284	201	7.077	0.034	3c	200.6	8.107	0.021
	0.0591	25.8	22.206	0.078	3b	26.7	13.947	0.12
	0.0591	40.9	20.616	0.142	3b	41.5	13.104	0.105
	0.0591	59.3	19.174	0.081	3b	59.7	12.135	0.123
	0.0591	79	17.994	0.09	3b	78.5	11.288	0.069
	0.0591	100.3	17.168	0.384	3b	99.2	10.551	0.123
	0.0591	151	14.598	0.064	3b	149.8	8.993	0.042
	0.0591	198.2	12.789	0.008	3a	200.3	7.754	0.016
	0.0591	26.4	21.06	0.056	3d	26.5	15.177	0.104
	0.0591	40.9	19.689	0.12	3d	41.5	14.141	0.044
	0.0591	59.4	18.216	0.079	3d	60.3	13.085	0.087
	0.0591	78.8	17.138	0.073	3d	79.2	12.287	0.041
	0.0591	100.8	16.168	0.112	3d	100.1	11.454	0.025
	0.0591	150.4	13.894	0.064	3d	148.9	9.694	0.019
	0.0591	199.4	12.167	0.037	3d	200.2	8.315	0.007

Figures 21 and 22 summarizing the diffusivity measurement results show that the high volume fractions (8.0v% and 5.91v%) of stitched nanotube yarns have noticeable impact on the diffusivity values of the resultant C/C composites, compared to their control samples. The control samples also show consistent diffusivity values.

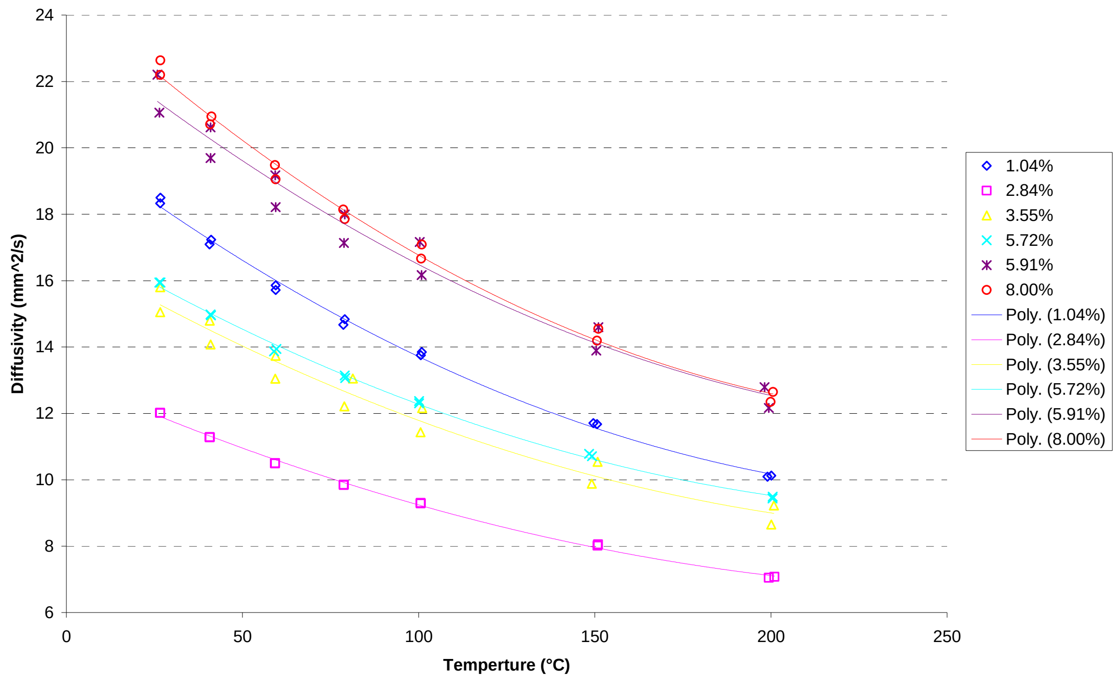


Figure 21. Diffusivity vs. volume fractions of stitched nanotube yarns

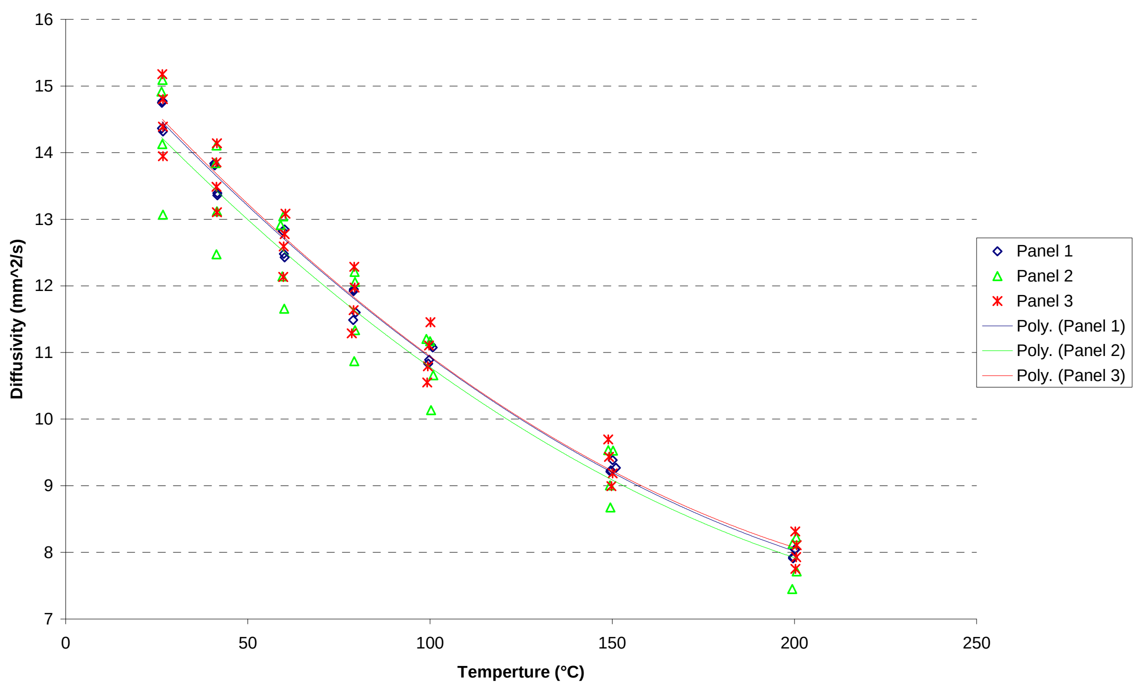


Figure 22. Diffusivity of the control samples

6.3 Thermal conductivity calculation and discussion

Thermal conductivity values of the samples were calculated based on Equation 2. Major parameters were:

$$K_{eff}(T) = \alpha(T)\bullet cp(T)\bullet \rho(T) \qquad (2)$$

cp = 0.71128 J/gK (value provided by Allcomp Inc.)

ρ = Tables 5 and 6 (less that 1% variability for controlled samples)

α = Table 7-9

Figure 23 shows the thermal conductivity values at room temperature of all the samples. The results reveal some potential outliers in the data. The controlled samples had an average Kz between 16-17 W/mK, and stitched samples with 2.84v%, 3.55v%, and 5.72v% stitching CNT yarns appear to lie below that value and considered as potential outliers. Figure 5 compares stitched samples to control samples cut from the same region of their particular panel. It can be seen that the C/C composites samples of 1.04v%, 5.91v% and 8.00v% stitching nanotube yarns show noticeable Kz increase as expected. The C/C composite samples with 8wt.% stitched nanotube yarns show the Kz as high as 24.5W/mK, which is about 44% increase compared to 17 W/mK conductivity of the control sample. These outlier samples may be due to low density and high void contents as discussed in Section 6.1.

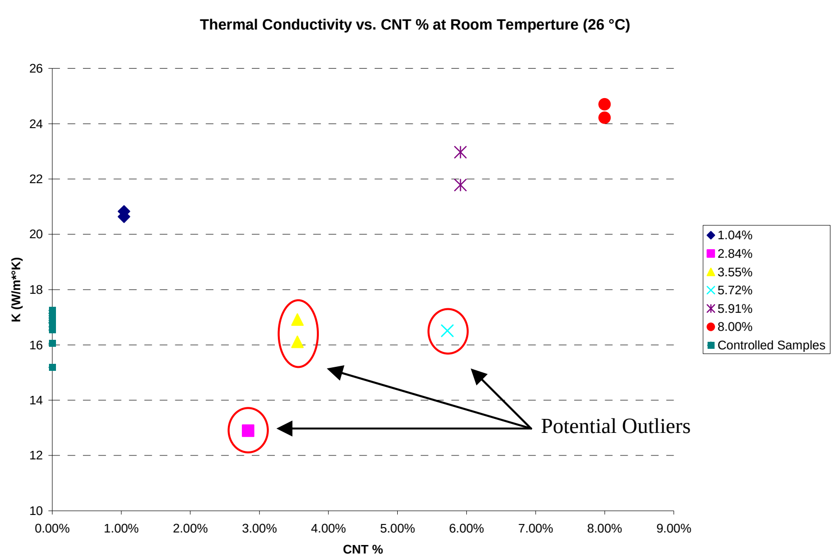


Figure 23. Thermal conductivity of all samples at room temperature

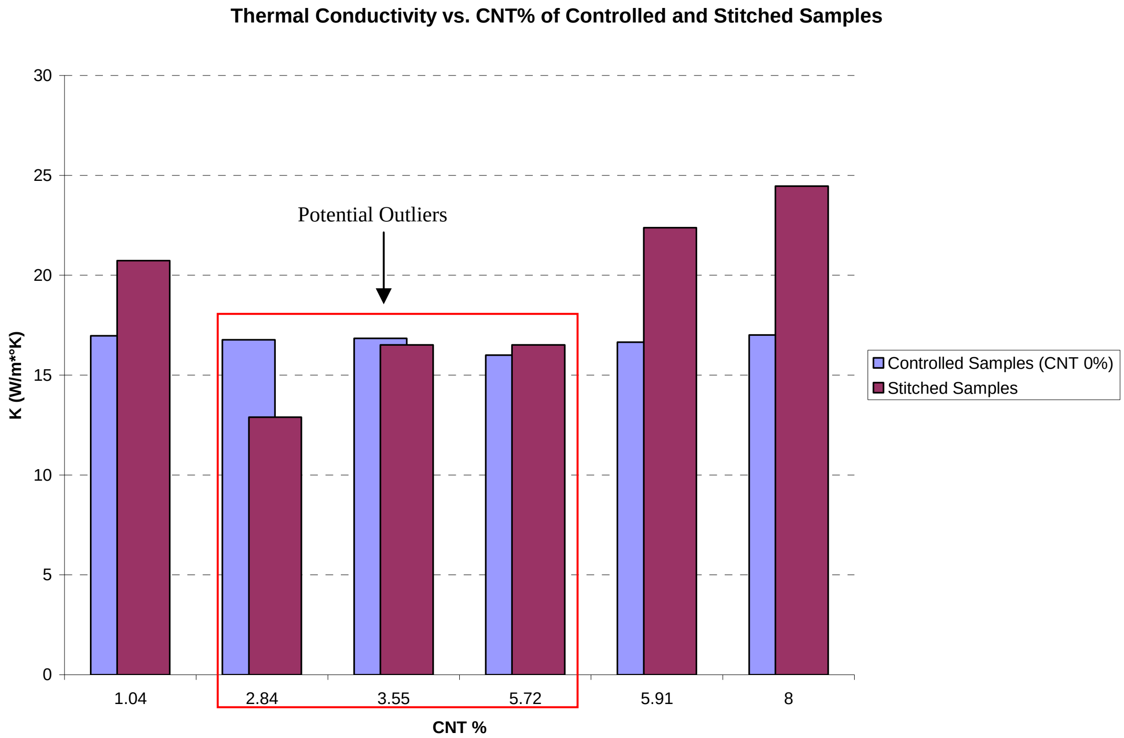


Figure 24. Thermal Conductivity of the stitched samples compared to their neighbor controlled samples

6.4 Prediction of the thermal conductivity of nanotube yarns

Rule of Mixture was used to reveal the thermal conductivity of the nanotube yarns used in the experiments:

$$K_{eff} = K_{cc} \cdot (1 - v_f) + K_y \cdot v_f \qquad (3)$$

K_{eff} = Effective Thermal Conductivity of the Stitched Samples (Measured Values)
K_y = CNT Yarn Thermal Conductivity
K_{cc} = Carbon-Carbon Composite Conductivity of the Controlled Samples (Measured Values)
v_f = Volume Fraction of Stitched Nanotube Yarns

Table 10 shows the predicted results of the nanotube yarn conductivity based on the experiments results. The conductivity of the nanotube yarns was in the range of 111-375 W/mK.

Table 10. Thermal conductivity prediction of nanotube yarns

Rule of Mixture			
K_{cc} (W/mK)	v_f	K_{eff} (W/mK)	K_y (W/mK)
17.0	1.04%	20.7	375
16.8	2.84%	12.9	-
16.8	3.55%	16.5	-
16.0	5.72%	16.5	-
16.7	5.91%	22.4	113
17.0	8.00%	24.5	111

7. SEM Analysis

High-resolution SEM images of fractured surfaces of the C/C composite samples were conducted to investigate nanostructures, the carbon matrix adhesion to the CF and CNTs, and the survivability of nanotubes. The SEM machine used was a JOEL 7401F model. Figure 25 shows the stitched nanotube yarns existed in the resultant C/C composite samples, indicating the survival of nanotubes after C/C composite manufacturing and high process temperatures (~2800°C). Figure 26 shows large voids existing around the stitched nanotube yarns in the C/C composites, which may be the reason for the three outlier data of thermal conductivity measurements for the stitched samples.

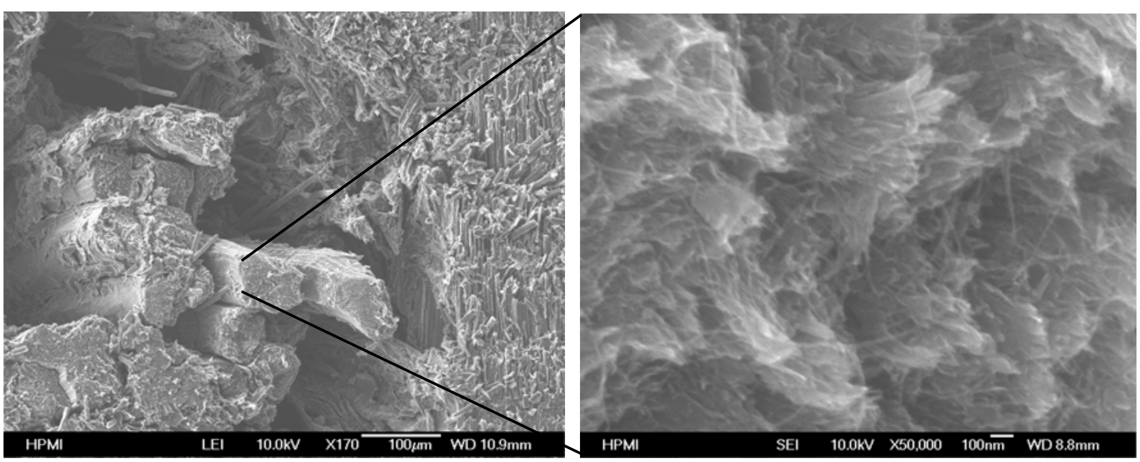


Figure 25. Stitched nanotube yarns in the C/C composite sample

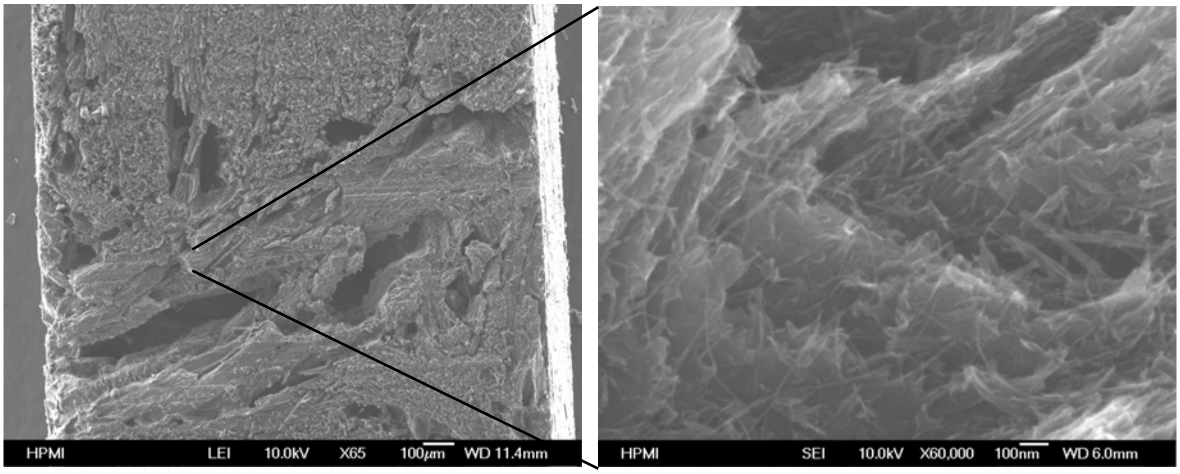


Figure 26. Void around stitched nanotube yarns in the C/C composite sample

8. Conclusion

This research demonstrated a novel method to stitch carbon nanotube yarns along the through-thickness direction of carbon fiber two-dimensional precursor felt perform to make novel 3D reinforced carbon/carbon (C/C) composites. By stitching nanotube yarns, high strength and thermal conductive CNTs were incorporated into the preform to significantly reinforce and improve thermal conductivity along the thickness direction. The C/C composite samples with 1wt.%-8wt.% stitched nanotube yarns were fabricated using T300 plane weave precursors and in situ densification process. The C/C composite samples with 8wt.% stitched nanotube yarns showed the Kz as high as 24.5W/mK, which is about 44% increase compared to 17 W/mK conductivity of the control sample. Using the Rule of Mixture, the conductivity of the nanotube yarns used was estimated in the range of 110W/mK~375W/mK. SEM and Raman analysis also proved the survivability of nanotubes after 2500°C~2800°C consolification and carbonization processing temperatures. These results demonstrate the feasibility of using stitched nanotube yarns to effectively improve through-thickness conductivity.

Three minority students (one graduate and two undergraduate students) were involved in the project. During project, one student graduated with MS degree, and one entered into MS program. The research team successfully completed all planned research as well as involvement and exposure of minority students for cutting-edge nanomaterials and nanotechnology research. We also attracted and motivated minority students for high-degree study in the areas of scientific and engineering research and development.

In 2008, we sent two students to present posters at the AFRL HBCU annual review meeting at New Orleans. A conference paper titled “Thermal Management of Increasing Through-Thickness Thermal Conductivity of Fiber-Reinforced Composites” was presented at NATAS 2008 Conference, Atlanta, Georgia, August, 2008. One journal paper manuscript is being prepared.

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